Full Paper

Cyclic Voltammetric Behavior of Nitrogen-Doped Tetrahedral Amorphous Carbon Films Deposited by Filtered Cathodic Vacuum Arc

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Abstract
Nitrogen-doped tetrahedral amorphous carbon (ta-C:N) films were deposited by filtered cathodic vacuum arc (FCVA) technique using nitrogen as a background gas. The structure of the ta-C:N films was studied with X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy in terms of nitrogen flow rate used during the film deposition. Potential windows of the films measured in deaerated and unstirred solutions, such as 0.5 M HCl, 0.1 M KCl, 0.1 M NaCl, 0.1 M KOH, and 0.1 M NaOH, were about 2.4, 2.32, 3.2, 3.1, and 3.25 V, respectively. This study showed that the potential windows of the ta-C:N films were also affected by nitrogen flow rate. The ta-C:N films used in this study had the desired voltammetric characteristics suitable for electrochemical analysis.

1. Introduction

Diamondlike carbon (DLC) films are attractive for electronic, optical, mechanical, electrochemical, and biomedical applications because of their excellent properties such as high hardness, low coefficient of friction, high wear and corrosion resistance, high thermal conductivity, and high optical band gap.

In DLC films, sp^3 bonds are responsible for the mechanical properties whereas sp^2 bonds control the optical and electronic properties of the films [1]. Addition of nitrogen into DLC films can modify the properties of the films. For example, N incorporation could lower the residual stress [2] and increase the electrical conductivity of DLC films [3].

That N incorporation could lower the resistivity of DLC films was possibly attributed to that the doped N had raised the Fermi level towards the conduction band and narrowed the band gap by graphitization of the bonding structure [4]. Zeng et al. also proposed that the conductivity of DLC films could be increased by: i) a broadened conduction band or a downward shift of the Fermi level and ii) an increase in the density of states at Fermi level and in band tails [5].

Electrochemical application of DLC films depends largely on their adhesion to substrates along with some other functional properties. A sufficient adhesion strength of a film to its substrate can lessen the undermining effects of corrosive mediums and increase its chemical and electrochemical performances.

Cyclic voltammetry (CV) is one of the most frequently used electrochemical methods because of its relative simplicity and high information content. CV has a great advantage for elucidating the mechanisms of electrode reactions that are complicated by chemical (C) reactions that either precede or follow the electron (E) transfer steps, such as EE, EC, CE, and ECE, etc. which are important to consider when multiple peaks or strange-looking CV waves are encountered experimentally. CV is attributed to overall currents composed primarily of four components: i) expected Faradic current from electrochemical reactions, ii) charging current, iii) variable current from electrochemical reactions of electrode surface, and iv) trace current from electroactive impurities in solution. Various studies on the cyclic voltammetric behavior of nitrogen-doped DLC films in acidic solutions have been reported [5–8]. Yoo and co-workers reported that nitrogen-incorporated DLC film electrodes could have a wider electrochemical potential window in a $HClO_4$ solution than boron-doped diamond coatings [6]. The electrochemical kinetics of Cu(I)/Cu(II) redox reaction on nitrogen-doped DLC films was also addressed with voltammetry [7]. Lagrini et al.'s work showed that nitrogen-doped DLC films tested in a $LiClO_4$ solution had potential windows from 3.2 to 3.6 V [8]. Zeng et al. also reported that nitrogen-doped DLC films tested in H_2SO_4, $HClO_4$ and HCl solutions had potential windows of 3.41, 2.95 and 1.93 V, respectively [5].

This paper is to study the voltammetric behavior of nitrogen-doped tetrahedral amorphous carbon (ta-C:N)

thin films, deposited via a filtered cathodic vacuum arc (FCVA) process, tested in an acidic solution of HCl, neutral solutions such as KCl and NaCl, and hydroxide solutions such as NaOH and KOH.

2. Experimental

Boron doped highly conductive p-type (111) silicon wafers ($1 - 6 \times 10^{-3}$ Ωcm) were used as the substrates which were first cleaned in a detergent liquid and then in deionized water using an ultrasonic machine before placed in the vacuum chamber. The substrate surfaces were further etched by Ar^+ ions bombardment in the vacuum chamber prior to film deposition to remove the oxide layers. After the plasma etching, the ta-C:N films were deposited on the substrate surfaces by means of a filtered cathodic vacuum arc (FCVA) system (Nanofilms) using a pure graphite ($\geq 99.9\%$ C) target as the C source at different N_2 flow rates from 3 to 20 sccm and a fixed pulse bias of 1,500 V applied to the substrates. The thicknesses of the ta-C:N films were approximately 100 nm.

The film elemental composition was determined by X-ray Photoelectron Spectroscopy (XPS) (Kratos Axis Ultra) using a pass energy of 160 eV for survey scans and 40 eV for C 1s, N 1s and O 1s core level spectra. The X-ray source used was a monochromatic Al K_α line ($hv = 1486.71$ eV).

The structure of the films was investigated with Confocal Micro Raman Spectroscopy (Renishaw S2000) using a line of 632 nm excited by a He-Ne laser over the range of 800 – 2000 cm^{-1}. An objective lens ($\times$ 50) was used for a better signal-to-noise ratio. The Raman instrument had a spectral resolution of 1 cm^{-1} and a spatial resolution of 1 μm.

The adhesion of the films was evaluated with a micro scratch tester (Shimadzu SST-101) operated in a progressive mode, where a stylus with a diamond tip of 15 μm in radius was brought into contact with the sample surface and then dragged across a specified distance with a gradually increased load at room temperature. The scratch scanning amplitude was set at 50 μm with frequency of 30 Hz, scan speed of 10 μm/s and down speed of 2 μm/s for all the tests. Five measurements per sample were taken to get an average value of critical load.

Atomic force microscopy (Digital Instruments S-3000) operated with a Si_3N_4 cantilever in tapping mode was used to measure the surface topography (scan size of 1×1 $μm^2$) of the ta-C:N films.

Cyclic voltammetric (CV) experiments of the ta-C:N films were carried out in deaerated and unstirred solutions such as HCl, KCl, NaCl, KOH, and NaOH with a bionano electrochemical workstation (LK6200) having a potential resolution of 0.1 mV and a current resolution of less than 0.1 pA. The voltammograms were acquired using three electrodes immersed in a flat cell kit containing an electrolytic solution with a scan rate of 100 mV/s at room temperature. For the electrochemical testing, the ta-C:N film coated samples were cut into 2 cm $\times$ 2 cm square pieces, and a gold layer was deposited on the backsides of the Si substrates to make the testing samples in good electrical connection. The testing area on the films was a circle of 1 cm in diameter. The potentials were measured with respect to a standard saturated calomel reference electrode (SCE) in a saturated KCl solution (244 mV at 25 °C), and a platinum mesh was used as the counter electrode. The electrochemical kinetics of the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ redox reaction on the ta-C:N film was investigated in a deaerated and unstirred 5 mM $K_3Fe(CN)_6$/0.1 M NaCl solution. The potential was scanned from -0.3 to 0.8 V with different scan rates of 30, 50, 70, 90, 110, and 130 mV/s. All the chemicals employed in this study were analytical reagent grades.

3. Results and Discussion

3.1. Structure of ta-C:N Films

Figure 1 shows the Raman spectra of the ta-C:N films deposited under different nitrogen flow rates. All the Raman spectra of the ta-C:N films show a near symmetrical band centered at approximately 1523 cm^{-1}. Normally, the sp^2 sites mainly exist as chains rather than aromatic rings in the ta-C films, in that they do not apparently give rise to a D peak in a Raman spectrum [9]. The nitrogen doped in the DLC films can adopt many bonding configurations in carbon networks, resulting in a variety of structures and promoting the formation of sp^2 sites in the films [10]. Therefore, the shapes and peak positions of the corresponding Raman spectra can be obviously different for the ta-C:N films deposited with different nitrogen flow rates. It is found that the asymmetry of the Raman bands increases with nitrogen flow rate, which is due to increased bond-angle and bond-length disorders which in turn broaden the Raman spectra of the films. Although the Raman spectra have no apparent D peaks, they were deconvoluted using a Gaussian function for G peak and a Lorentzian function for D peak in order to investigate the correlations of peak intensities (I_D/I_G) and peak areas (A_D/A_G) to the effect of nitrogen doping, where I_D and A_D are respectively the intensity and integrated area of the D peak, and I_G and A_G are respectively the intensity and integrated area of the G peak. The I_D/I_G and A_D/A_G ratios change from 0.97 to 1.23 and from 2.05 to 2.76, respectively, with the nitrogen flow rate being changed from 3 to 20 sccm. The increases of the I_D/I_G and A_D/A_G ratios reveal increased clustering of sp^2 phases and decreased sp^3 fraction [11, 12]. N not only increases the number of sp^2 sites but also causes the existing sp^2 sites to cluster in the ta-C:N films, resulting in a reduced band gap through graphitization as reported in literature [13].

Microscratch measurements were carried out in order to evaluate the adhesion strengths of the ta-C:N films in terms of critical load at which the adhesive failure of the films to the substrates occurs. An average value of the critical load increases approximately from 448 to 477 mN with nitrogen flow rate. Sullivan et al. [14] reported that shorter sp^2 bonds than sp^3 bonds could reduce the strains inside DLC films.

The increased sp^2 bonds, especially C=N bonds, induced by N incorporation can decrease the residual stress of the ta-C:N films. The C=N bonds are expected to be efficient to reduce the residual stress of the films because C=N has a shorter bond length of 1.29 Å compared to either C–C (1.54 Å) or C=C (1.34 Å) [15].

The surface roughness of the ta-C:N film (3 sccm N_2) has finer asperities as shown in Figure 2a, which is due to a large percentage of sp^3 carbon bonding formed by the high impinging carbon energy during deposition [16]. This can also be clearly indicated by its R_{sk} (0.267) and R_{ku} (4.307) values. It is a peak biased surface with a large number of spike peaks because the R_{sk} value is positive and the R_{ku} value is greater than 3. Larger-sized asperities can be observed on the ta-C:N film (20 sccm N_2) in Figure 2b. The surface having $R_{sk} = 0.026$ and $R_{ku} = 2.857$ is also a peak biased surface with a large number of nearly round peaks because the R_{sk} value is positive and the R_{ku} value is smaller than 3. These features are caused possibly by the N doping in the film or nitrogen normal bonding [8, 9] and an increased number of sp^2 sites with the increased nitrogen flow rate decreases the densification of the films [17, 18]. The aggregation of the nitrogen inclusion in the film also contributes to the surface roughness of the film due to the difference in electronegativity values between the carbon (ca. 2.55, pauling scale) and nitrogen (ca. 3.04).

3.2. Cyclic Voltammetry of Acidic Solution

The cyclic voltammograms of the ta-C:N film electrodes measured in a 0.5 M HCl solution at a scan rate of 100 mV/s are illustrated in Figure 3. A difference between the potentials for hydrogen and oxygen evolutions in a cyclic voltammogram gives an electrochemical potential window. The wider the potential window, the more the elements in the solutions can be detected for metal tracing analysis. The potentials for hydrogen and oxygen evolutions on the surface of the ta-C:N film electrode (3 sccm N_2) are about -1.25 V and $+1.15$ V, respectively. The ta-C:N film electrode (20 sccm N_2) has a lower negative potential value of about -0.8 V for hydrogen evolution. It is clearly seen that the potential window of the films decreases with increasing nitrogen flow rate [8, 19], which can be explained in terms of electrical resistivity of the films as nitrogen doping reduces the electrical resistivity of the ta-C:N film electrodes [4, 20]. The promoted electrical conductivity reduces an electron transfer potential through the ta-C:N film electrode and results in early hydrogen evolution ($2H^+ + 2e^- \rightarrow H_2 \uparrow$) at a lower negative potential value in the reduction. From the cyclic voltammogram in Figure 3, no change in potential for the oxygen evolution ($4OH^- \rightarrow 2H_2O + O_2 \uparrow + 4e^-$) is found in the oxidization half cycle at the scan rate of 100 mV/s. It is clearly found that the potential window is mainly affected by the potential for the hydrogen evaluation in the acidic aqueous solution where the main influent ions are H^+ ions. A contribution of background current to the cyclic voltammogram of the ta-C:N film electrode (3 sccm N_2) can be
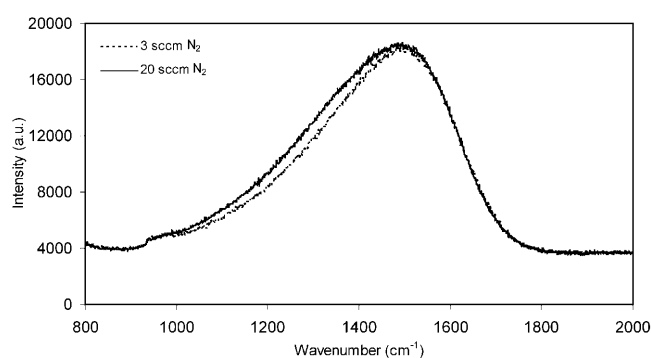

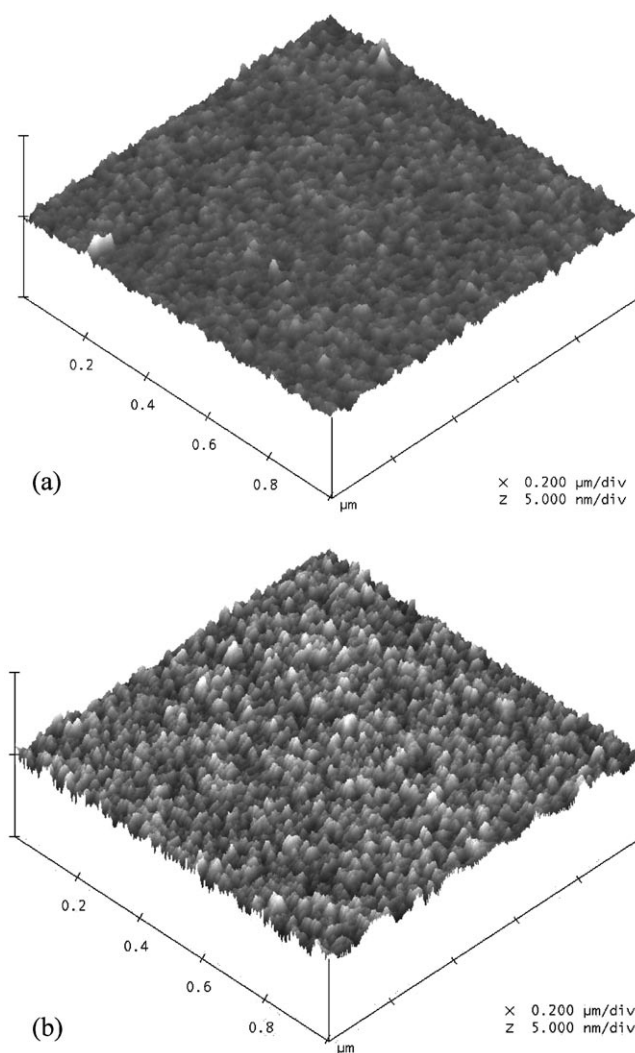Fig. 1. Raman spectra of ta-C:N films with different nitrogen flow rates.

Fig. 2. AFM images of ta-C:N films with different nitrogen flow rates: a) 3 and b) 20 sccm N_2.

found. The background current at solid electrode results from extraneous processes primarily associated with the electrode surface. Thus, according to the past history of the electrode, the surface may have become oxidized. The
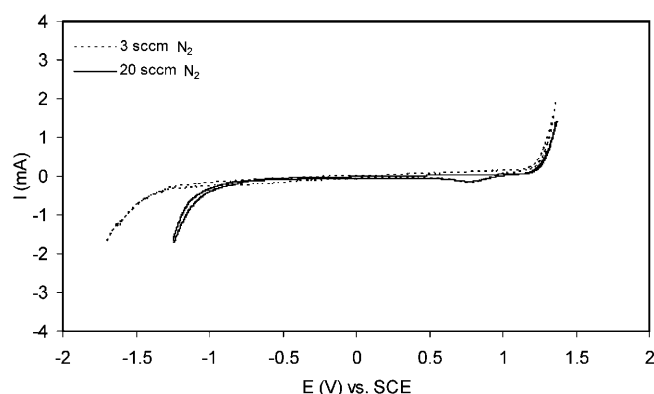
Fig. 3.   Cyclic voltammograms of ta-C:N film electrodes with different nitrogen flow rates measured in 0.5 M HCl solution at a scan rate of 100 mV/s.
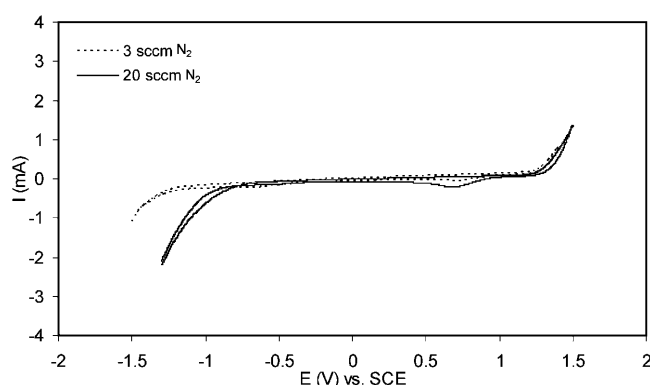

Fig. 4.   Cyclic voltammograms of ta-C:N film electrodes with different nitrogen flow rates measured in 0.1 M KCl solution at a scan rate of 100 mV/s.

potential applied to the electrode may then give rise to a current from the dissolution of the oxides. An XPS quantitative analysis of the stoichiometry of the ta-C:N film electrode surfaces indicates that the ta-C:N film electrodes (3 sccm N_2) have a higher surface oxygen fraction than the film electrodes deposited with 20 sccm N_2. This results from a higher affinity of oxygen with carbon since there is a greater difference in electronegativities between oxygen (ca. 3.44, pauling scale) and carbon (ca. 2.55) with respect to nitrogen (ca. 3.04). Thus, it can be deduced that the background current is mainly attributed to the dissolution of the oxidized layers. The occurrence of the peak observed in the reduction cycle may be due to the catalytic activity for Cl_2/Cl^- [5, 6].

3.3. Cyclic Voltammetry of Neutral Solutions

Figure 4 shows the cyclic voltammograms of the ta-C:N film electrodes tested in a 0.1 M KCl (pH 1) solution at a scan rate of 100 mV/s. The pH value of the solution was adjusted by HCl ($HCl \rightarrow H^+ + Cl^-$). The effect of nitrogen incorporation on the potential windows of the ta-C:N film electrodes in the solution can also be seen. The film electrodes deposited with 3 and 20 sccm N_2 have potential windows of approximately 2.32 V and 1.9 V, respectively. The potential window decreases with increased levels of the incorporated nitrogen, resulting from the increased electrical conductivity. This is in agreement with the result mentioned in the preceding section where the contribution of the background current was attributed to the dissolution of the oxidized layer on the ta-C:N film electrode (3 sccm N_2). It is noticed from this experiment that a higher nitrogen content in the ta-C:N film electrodes produces a lower background current leading to an improved signal-to-background ratio in the electroanalytical measurement. The ta-C:N film electrode produces a lower potential window in the 0.1 M KCl solution even with pH 1 compared with the electrode tested in the 0.5 M HCl solution. This may be due to more concentrated active H^+ ions in the HCl solution.

It has been shown that the nitrogen flow rate apparently affects the potential windows of the ta-C:N film electrodes in the KCl and HCl solutions. The ta-C:N film electrodes (20 sccm N_2) are used for further analysis of the electrochemical potential windows in different solutions in order to investigate their outstanding electrochemical properties. The cyclic voltammogram of the ta-C:N film electrode (20 sccm N_2) recorded in a 0.1 M NaCl solution with a scan rate of 100 mV/s is shown in Figure 5. The pH value of the NaCl solution is not compensated by HCl. The potential window of the ta-C:N film electrode (20 sccm N_2) in the NaCl solution is approximately 3.2 V, about 1.3 V higher than the potential window of the same electrode measured in the KCl aqueous solution. The difference in potential window can be explained by different pH values. The KCl solution compensated by HCl has a higher concentration of active H^+ ions than the NaCl aqueous solution uncompensated by HCl. Both unbalanced hydrogen and hydroxide ions and different electroactive species existing in the KCl and NaCl aqueous solutions can abruptly affect the cyclic voltammetric behavior of the ta-C:N films in the solutions. No peak occurring in the reduction half cycle measured in the NaCl solution indicates a lower catalytic activity for Cl_2/Cl^- in the solution, which may be one of the reasons why the cyclic voltammogram in the NaCl solution has a lower potential window.

3.4. Cyclic Voltammetry of Hydroxide Solutions

Figures 6 and 7 show the cyclic voltammetric $I-E$ curves of the ta-C:N film electrodes (20 sccm N_2) recorded in 0.1 M KOH and 0.1 M NaOH solutions at a scan rate of 100 mV/s. The ta-C:N film electrode tested in the NaOH solution has a higher potential window of approximately 3.25 V compared to approximately 3.1 V measured in the KOH solution. This may be attributed to different electroactive alkaline species of the solutions. The potential windows of the ta-C:N film electrodes in the solutions containing a higher concentration of OH^- ions are higher, compared to those of the film
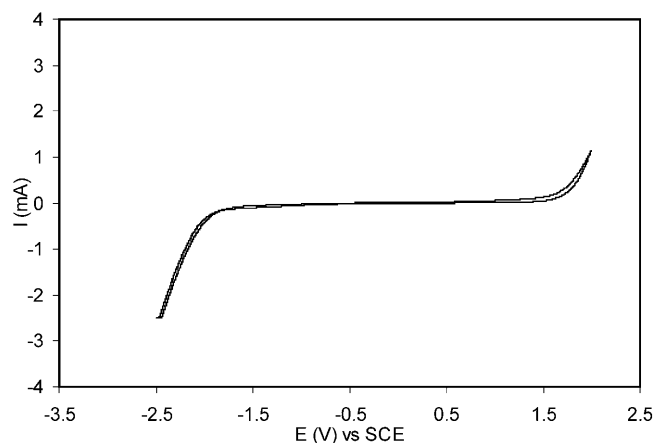
Fig. 5. Cyclic voltammogram of ta-C:N (20 sccm N_2) film electrode measured in 0.1 M NaCl solution at a scan rate of 100 mV/s.
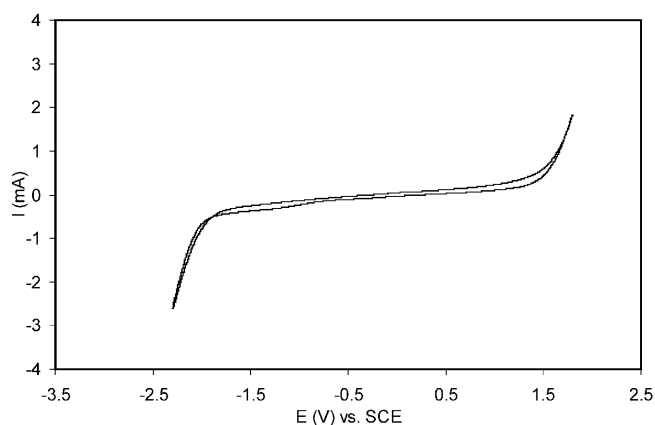

Fig. 6. Cyclic voltammogram of ta-C:N (20 sccm N_2) film electrode measured in 0.1 M KOH solution at a scan rate of 100 mV/s.

electrodes in the solutions containing a higher concentration of H^+ ions. This can be explained by acid-base reactions in which H^+ ions and OH^- ions are mainly involved. An alkaline hydroxide (KOH, NaOH) dissociates into a cation and one or more hydroxide ions in water, making the solution basic. These hydroxide ions react with hydrogen ions to form water ($OH^- + H^+ \rightarrow H_2O$), resulting in a decrease in acidity of the solution. Hydrogen evolution lately occurs in a hydroxide solution containing a low concentration of active H^+ ions, resulting in a wider potential window. A background current attributed to the charging effect of electric double layers can be seen on both the cyclic voltammograms of the ta-C:N films measured in the KOH and NaOH aqueous solutions. The OH^- ions decomposed from KOH or NaOH near the electrode combine with hydronium ions (H_3O^+) to form water molecules ($OH^- + H_3O^+ \rightarrow 2H_2O$) which lead to an adsorbed water layer on the electrode surface and a water hydration sheath surrounding the ions, resulting in the separation of the charges. Because the charging effect is
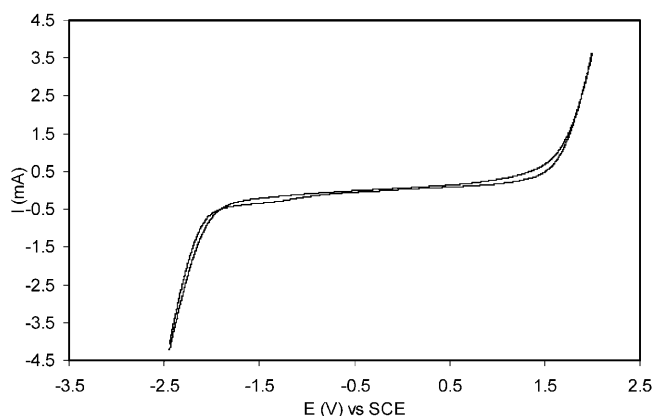

Fig. 7. Cyclic voltammogram of ta-C:N (20 sccm N_2) film electrode measured in 0.1 M NaOH solution at a scan rate of 100 mV/s.

becoming greater with increasing the concentration of the OH^- ions, the cyclic voltammograms of the ta-C:N film electrodes measured in the hydroxide solutions have higher backgrounds attributed to the electric double layers.

3.5. Cyclic Voltammetry of Reversible Couple (Ferricyanide)

Figure 8 shows the scan rate dependence of the cyclic voltammograms measured at the ta-C:N film electrodes (20 sccm N_2) using the reversible ferri-ferrocyanide couple as a redox system [8]:

$$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$$
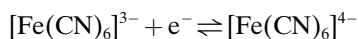
The electrolyte used was 0.1 M NaCl with pH 1 compensated by H_2SO_4. It is found that ΔE_p value increases from 92 to 124 mV when the scan rate is increased from 30 to 130 mV/s. This is due to the effect of the increased kinetic
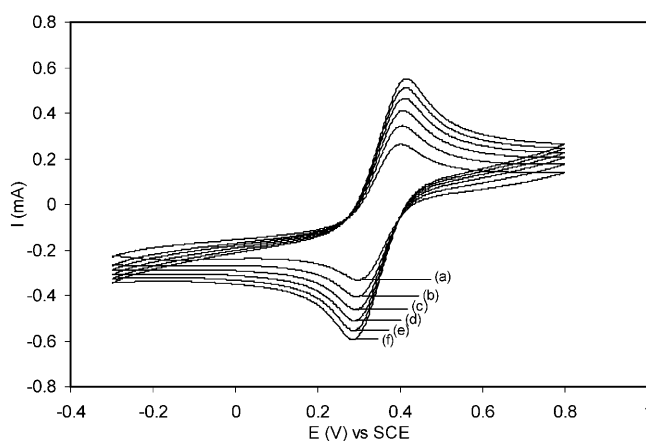

Fig. 8. Cyclic voltammograms of ta-C:N (20 sccm N_2) film electrode measured in 5 mM $K_3Fe(CN)_6$/0.1 M NaCl solution at different scan rates: a) 30, b) 50, c) 70, d) 90, e) 110, and f) 130 mV/s.

limitation to shifting an oxidation to more positive potentials and a reduction to more negative potentials [21]. As the scan rate is increased, the timescale of the experiment becomes smaller so that, eventually, an equilibrium is not reached at the film electrode surface and a kinetic effect begins to appear. It is found that the ratio between anodic and cathodic current peaks ($I_{p,a}/I_{p,c}$) fluctuates between 1.02 and 1.06. An $I_{p,a}/I_{p,c}$ ratio slightly greater than unity indicates that the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ redox reaction at the ta-C:N film electrode exhibits a quasireversible behavior, which means that though the reverse peak appears, it is slightly smaller than the forward one [5].

4. Conclusions

The influence of the nitrogen incorporation in the ta-C:N films on the structure and electrochemical behavior of the films was investigated. The Raman results showed that the sp^2 sites in the films increased with nitrogen flow rate and the increase in sp^2 sites increased the surface roughness of the films. Although the ta-C:N film electrodes offered i) wide potential windows with different types of solutions, ii) very low and stable background currents to improve the signal-to-background and signal-to-noise ratios, iii) repeatability of voltammograms (durability of the ta-C:N film electrode to high anodic potential) and iv) long-time response stability, their voltammograms were apparently affected by their electrical conductivity, type of alkaline species and unbalanced H^+ and OH^- ions. It was found that the background current was attributed to not only the concentration of OH^- ions but also the surface cleanliness (surface oxidized layer). Finally, it can be concluded according to the experimental findings that the ta-C:N film electrodes prepared by FCVA had outstanding properties for electrochemical application.

5. References

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